A PROCEDURE FOR THE SYSTEMATIC MICROANALYSIS OF CATIONS

BY

MARY OLIVE HILLIS

A. B., Mac Murray College for Women, 1941

M. S., University of Illinois, 1942

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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A PROCEDURE FOR THE QUALITATIVE MICROANALYSIS OF CATIONS

I. Introduction

During the last two decades, spot tests have been used successfully for the identification of cations in simple mixtures, but they have not, to any great extent, been used in systematic analysis other than for confirmatory tests.

Numerous investigators have developed schemes of analysis using spot reactions. Some have attempted with varying degrees of success, to avoid group separations altogether; some have used separations without the use of sulfides; others have taken the H_2S system as their basis.

The original purpose of this investigation was to work out a scheme of cation analysis using organic reagents as group precipitants. When the results of this experimentation proved unpromising, the study of the use of inorganic precipitants, other than H_2S or related compounds, was undertaken. This method was found inferior to the H_2S system.

It was decided that the classical H_2S system, although in many ways far from desirable, probably offers the best method for group separations. In this investigation an attempt has been made to shorten and simplify the classical system by substituting spot reactions for the usual separation of ions within a group.

II. Historical

Microanalysis is a very old branch of chemistry, dating back at least to the beginning of the Christian era. Some of the earliest chemical reactions in the wet way were tests which today would be classed as spot tests.

Microscopic analysis, an important branch of microanalysis, had its start in the eighteenth century. Important work in this field has been done by Maggraf, Raspail, Helwig, Harting, Wormley, Boricky, Haushofer, Behrens, Schoorl, and, in later years, Emich, Deniges, Kleg, Chamot, and Benedetti Pichler.

Although many very early tests belong to the branch of microanalysis known as spot analysis, the true development of this field has taken place mainly within the last two decades, under the guidance of Fritz Feigl[1] and co-workers.

The use of spot reaction methods for systematic analysis was first suggested by Hauser[2]. Systems of analysis applying spot tests to the H_2S system have been established by von Nieuwenburg[3], Engelder and Schiller[4], Winkley, Yanowski, and Hynes[5], Davies[6], and Dobbins and Southern[7]. Schemes which make some use of H_2S but do not follow the classical system have been proposed by Heller[8] and Emschwiller and Charlot[9]. H_2S-less systems have been presented by Gutzeit[10], Gerstenzang[11] and Charlot and Bezier[12].

III. Investigation of Group Precipitants Other Than H_2S

The reactions of thirty-eight organic reagents with the common cations were investigated. It was hoped to find some organic reagents which would quantitatively precipitate the cations in groups of suitable size. Each group was to be precipitated from a separate small portion of the original solution in order to avoid interaction of the various organic compounds in the filtrate. None of the reagents studied was very promising, since most of them at any one pH, precipitated some ions quantitatively but others only partially, and, when present in small amounts, not at all. Some reagents precipitated groups that were too large to be of use and others formed precipitates that were difficult, if not impossible, to filter. It also seemed impossible to find suitable reagents which would make possible the inclusion of each ion in some group.

A method of analysis, based upon the detection, in the original solution, of certain ions or groups of ions, by use of specific or selective reagents, also proved unsuccessful. Some ions may be detected in the original in this manner, but, at present, the number of specific and selective reagents known is insufficient for the detection of all ions in this way.

A system of analysis in which groups were separated by inorganic reagents, other than H_2S or related compounds, was developed. In this scheme the cations were separated into (1)

the insoluble chlorides (by HCl), (2) the insoluble carbonates and hydroxides (by NaOH, Na_2O_2, and Na_2CO_3, and (3) the amphoteric hydroxides and the alkalies (filtrate from (2)). No satisfactory method for the microdetection of the magnesium and alkaline earth ions in (2) could be found. The separations were inferior to those by H_2S and the large amount of sodium salts greatly reduced the sensitivity of the spot tests used.

IV. The Systematic Microanalysis of Cations Based Upon the H_2S System

This procedure was worked out using a solution containing approximately 0.05 mg. of each common metallic ion per ml. One ml. of solution was used for the complete analysis.

Group I is precipitated by dilute HCl and consists of AgCl, Hg_2Cl_2, $PbCl_2$. The precipitated chlorides are treated with 10% KCN and heated. The appearance of a black or gray color due to the free Hg, formed when Hg_2Cl_2 reacts with KCN, is sufficient test for $Hg_2^{\cdot\cdot}$. The hot solution, containing $Ag(CN)_2'$ and $Pb(CN)_2$, is tested for $Pb^{\cdot\cdot}$ and $Ag^{\cdot}$. p-Dimethylaminobenzylidene rhodanine, specific for $Ag^{\cdot}$ in the presence of cyanide, and 4,4′-tetramethyldiaminotriphenylmethane, which reacts with $Pb^{\cdot\cdot}$ after oxidation to PbO_2, are used for these tests.

Group II consists of the metallic sulfides precipitated from the filtrate from Group I after the acidity has been adjusted to 0.25M HCl. The precipitated sulfides are boiled with 72% $HClO_4$, which produces a white precipitate of H_2SnO_3 and H_3SbO_4 and takes everything else into solution. The precipitate is reduced to metallic Sn and Sb by Al wire in the presence of dilute HCl. These precipitated metals are boiled with conc. HCl, dissolving the Sn, but not affecting the Sb. A black residue is metallic Sb and is sufficient test for $Sb^{\cdot\cdot\cdot}$. The solution is tested for $Sn^{\cdot\cdot}$ by cacotheline. The perchloric acid solution of the other ions is diluted and the following tests are made:

$Pb^{\cdot\cdot}$:	Tetramethyldiaminotriphenylmethane (after conversion to PbO_2 by NaOH, Br_2-water, and NH_4OH)
$Hg^{\cdot\cdot}$:	$SnCl_2$ (Test is made on filtrate from Group I, before adjustment of acidity.)

$Cu^{\cdot\cdot}$:	Rubeanic acid
$Cd^{\cdot\cdot}$:	Dinitrodiphenylcarbazide plus NaOH plus KCN plus HCHO
$Bi^{\cdot\cdot\cdot}$:	Cinchonine-KI
AsO_4''':	$(NH_4)_2MoO_4$-HNO_3 plus heat

Group III [$Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, Fe_2S_3, CoS, NiS] is precipitated from the Group II filtrate by NH_4OH and H_2S. The precipitate is boiled with 72% $HClO_4$ which brings about complete solution and oxidizes the sulfides completely to sulfates. The ions are detected in the diluted perchloric acid solution by the following tests:

$Al^{\cdot\cdot\cdot}$:	Aluminon plus NH_4OH plus $(NH_4)_2CO_3$
Cr_2O_7'':	Diphenylcarbazide plus dil. H_2SO_4
$Zn^{\cdot\cdot}$:	$K_3Fe(CN)_6$ plus diethylaniline
$Mn^{\cdot\cdot}$:	$NaBiO_3$ plus conc. HNO_3
$Fe^{\cdot\cdot\cdot}$:	KSCN
$Co^{\cdot\cdot}$:	α-Nitroso-β-naphthol
$Ni^{\cdot\cdot}$:	Dimethylglyoxime plus NH_4OH

No satisfactory method for the analysis of Group IV ($Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$) in the very dilute solution was found. In more concentrated solution the following method works quite well. The filtrate from Group III is acidified and boiled to precipitate sulfur and sulfides. The filtrate from this treatment is made alkaline with NH_4OH, boiled, and the carbonates of the alkaline earths are precipitated by $(NH_4)_2CO_3$. The solution of the carbonates in dilute acetic acid is tested as follows:

$Ca^{\cdot\cdot}$:	Titan yellow plus NaOH
$Ba^{\cdot\cdot}$:	Sodium rhodizonate (Spot formed is insoluble in dilute HCl (1:20).)
$Sr^{\cdot\cdot}$:	Sodium rhodizonate (Spot formed is destroyed by the dilute HCl used above. If $Ba^{\cdot\cdot}$ is present, add a drop of K_2CrO_4 to prevent its reaction with the reagent.)

The Group V ions ($Mg^{\cdot\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$) are detected in the usual manner. Ammonium salts are removed from the filtrate from Group IV by evaporating and igniting with HNO_3. The residue, taken up in water, is tested for $Na^{\cdot}$, $K^{\cdot}$, and $Mg^{\cdot\cdot}$

by the zinc uranyl acetate, sodium cobaltinitrite, and p-nitrobenzene-azo-resorcinol tests, respectively. Ammonium ions are detected in a few drops of the original solution by treating with NaOH, heating and passing the distillate of NH_3 fumes into a tube containing Nessler's reagent.

This procedure was checked on forty-four unknowns. As described, it is best for microsolutions. If it is to be used on solutions containing macroquantities of the ions, these must be diluted or larger quantities of reagents must be used in making the group separations and in dissolving the precipitates formed.

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Vita

The author was born in Beardstown, Illinois, December 11, 1919. She received her elementary education in the Beardstown public schools and graduated from the Beardstown High School in 1937. Her undergraduate work was done at MacMurray College for Women, Jacksonville, Illinois, where she received the degree of Bachelor of Arts in 1941. She was awarded a University Scholarship for graduate work at the University of Illinois and received the degree of Master of Science from that institution in 1942. She held University Fellowships during the years 1942-3 and 1943-4. She is a member of the American Chemical Society, Phi Beta Kappa, Sigma Xi, Iota Sigma Pi, and Sigma Delta Epsilon.